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UNPUBLISHED PRELIMINARY DATA

Since the period of support from NASA rather overlapped the periods of our ONR support (at least the benefits derived from it did), we are submitting summaries of the work of the two appropriate periods which were written to the ONR in support of fund requests for subsequent periods. The NASA work is nowhere clearly delineated from the ONR work except possibly in the Deslattes source and modulated slit instrumentation.

Period I -- October 1, 1962 - September 30, 1963

Research done during this period can be headed under two major subject titles. One is the study of localized optical excitation in alkali halides with special emphasis on the correlation of absorption and radiative decay (luminescence). The α-center luminescence and the luminescence due to excited iodine ions, diluted in a KCl host lattice were two major projects. The search for correlations of absorption and emission of molecular ions diluted in KCl crystals is a minor project.

The second major project was an extension of the useful range of the vacuum monochromators to as high a photon energy as possible, with the aim of investigating the absorption and reflectivity of alkali halides and other inorganic salts deep into their fundamental absorption region. During this year time was spent on instrumentation, the construction of

a new light source as well as the decrease of unwanted scattered light in the spectral region of high photon energies beyond 11 ev.

The different topics that were investigated will be presented singly:

a) α-Center Luminescence (T. Timusk)

The interest in the α-center luminescence was stimulated by Timusk's work on the luminescence of pure alkali halides with light excitation in the intrinsic absorption region of these salts. ("Luminescence Study of Alkali Halides in the Vacuum Ultraviolet;" T. Timusk; Thesis, Cornell June 1962 and "Recombination Luminescence in Alkali Halides;" T. Timusk and W. Martienssen, submitted for publication in the Physical Review). This study on the radiation damage of alkali halides by UV light gave results which suggest as the excited state, from which the observed luminescence occurs, a situation which might exist after excitation of α-centers; that is, an exciton absorption near a negative ion vacancy. In order to prove this hypothesis Timusk studied the α-center luminescence of NaCl, KCl, KBr and KI during his 6-months stay here. The results confirmed the presumption in all four crystal types. Moreover Timusk studied the shape, halfwidth and position of the α-emmission in great detail. The most striking result was the enormous Stokes shift of 4 ev.

This investigation thus demonstrated that recombination

luminscence and α-center luminescence are identical. This fact may give a clue to the nature of the excited state involved which, because of the large Stokes shift, must be quite different from the excited state reached in absorption. As similar results are presently observed in different cases, a reconsideration of presently accepted models will be necessary and investigations of this type will help to do this. A preliminary report of this work was given at the New York meeting of the American Physical Society (Bull. Am. Phys. Soc. 7, 38, 1962). A summary of this work is in preparation for publication. Dr. Timusk left in February 1962 to continue similar research with Professor W. Martienssen in Frankfurt, Germany.

b) Optical Study of a Localized Impurity in Alkali Halides.

The optical absorption process at atomically dispersed iodine ions diluted in a KCl host lattice was studied in detail last year ("Ultraviolet Absorption of KI Diluted in KCl Crystals; H. Mahr; Phys. Rev. 125, 1510, 1962). This year the processes occuring after excitation through light in the iodine absorption bands were studied. Observed was a radiative decay (luminescence) with about 10% efficiency and in some cases a competing thermal release into the conduction band.

The emission and excitation spectra of the iodine

luminescence were studied in detail. The shape, halfwidth, and position of the emission bands were studied as a function of temperature and under various conditions of excitation with light absorbed within the iodine absorption bands. Three different luminescent processes were observed with Stokes shifts as large as 4 ev. It was concluded that after excitation the system relaxes to a new equilibrium. In this process some of the excitation is lost by nonradiative processes. The remainder comes from excited ions in different equilibrium positions, i.e., different excited states are reached in thermal equilibrium and it is these states which give rise to the measured emission bands. Competing thermal release out of the excited state was found at higher temperatures. In one case the electron is thermally excited into the conduction band. Vacancies present in the crystal trap the electrons, forming F-centers, which were observed in absorption. Warm-up or release through F-light reverses the process and the electrons are recaptured at ionized iodine sites, giving off their characteristic luminescence (phosphorescence). Glow-curves and rates of buildup and decay of these processes were studied. Through this ionization process an extremely simple system of donor plus trap is realized in an ionic crystal. All quantities can be determined quantitatively. The investigation is not quite completed.

A preliminary report of the luminescence work was reported

at the Baltimore meeting of the American Physical Society (Bull. Am. Phys. Soc. 7, 178, 1962) and a summary is in preparation for publication in the Physical Review. A preliminary report of the work on the ionization of electrons from iodine ions, their trapping and recapture was given at the International Color Center Symposium in Stuttgart, Germany August 21-24, 1962.

c) Construction of a New Light Source and Detection System. Professor P. L. Hartman, J. Powlette.

In an attempt to reach higher photon energies in our optical studies, a new detection system is being worked on along with a new light source. The detection system attempts to obviate the scattered light problem by modulating the entrance slit position thus getting from the exit slit an AC signal in the desired focused light, while the scattered light is largely unmodulated. The system works and some advantage is gained by working the AC light at the same frequency as the modulating frequency but more is gained by taking the second harmonic. The system has operated and now awaits arrival of a sensitive synchronous detector now on order, to test its ultimate capabilities. This work is planned to continue until the system is proved or disproved as satisfactory.

R. Deslattes at Cornell has investigated in the very far UV with a grazing incidence instrument, radiation produced

in a Penning discharge operating at fairly high currents. His results looked promising enough to warrant our building a similar source to look at the region 500-1000A. This has been done and preliminary results indicate it is not as good as the capillary discharge source we have been using, at least with Argon gas as the discharge medium in both cases. Sputtering is very rapid in the new source so life is short but we are not yet done with it. A new source in the 500-1000A region would be a great help to many workers.

A paper describing the two monochromators system has been accepted for publication and an invited review paper of our past work was given at the 1st International Vacuum Ultra-Violet Conference held last April in Los Angeles.

d) Minor Projects (T. Logothetis, S. Duckett)

As part of a combined project with Professor Pohl in this department the optical properties of molecules diluted in alkali halides were studied. It was found that alkali halides provide an excellent means of dilution for these molecules. Extremely sharp infrared spectra and ultraviolet absorption bands showing fine structure due to internal vibrations of the molecule were observed for the system NO_2^- and NO_3^- in KCl. A summary of this work, which is still in progress, will be published soon. As part of our general topic of the investigation of excited states, Duckett also searched for luminescence from excited NO_3^- and NO_2^- ions in

KCl. With the excitation used no luminescence was observed. In a different attempt O_2^- molecules diluted in KCl were investigated. Rolfe reported an extremely sharp fine structure of emission bands excited in the O_2^- absorption band. We looked for this fine structure in the absorption band, again to correlate both processes. This search was unsuccessful.

This whole program is part of an attempt to understand the interaction of normal mode vibration and electronic transitions in these simpler molecules. The search is for a molecule, which can be diluted in alkali halides and shows a clear-cut luminescence as well as absorption. This program will be continued with minor projects.

T. Logothetis worked on preparations for extending absorptions and reflectivity measurements into the region of very high photon energies. He discovered operating conditions for the old light source which gives higher light output in the far UV and he has built a new vacuum system for the detector chamber which will provide a higher pumping speed for the evaporation of thin layers to be used in the absorption measurements. He is presently starting to work on the general feasibility of the idea to measure the absorption of thin alkali halide films as the ratio of signals before and after the evaporation of alkali halide films directly onto a phosphor. In this way the impossibility of finding a transparent substrate for these photon energies will be avoided.

We have previously used this technique in studies on solid argon and on LiF.

J. N. Lloyd in the summer of 1961 made extensive measurements on the photoemission from LiF and has spent a fair part of this year (not in residence) analyzing the data and writing up the work. It is hoped that this will be published during the coming year. There are still some puzzling aspects remaining in this study which may yet be worth further investigation.

e) Ruby Laser (Professor Hartman, H. Mahr)

A ruby laser system was built this spring. The total system involves a power supply capable of charging a 300 μF capacitor to 5000 volts, a GE FT-564 flash tube and a crystal holder designed for sufficient cooling of the ruby crystal and sampling of the laser input. The system was mostly built here. Laser action was observed with a rather small threshold. The system will be used for the study of 2-photon processes as will be pointed out later.

Period II -- October 1, 1963 - September 30, 1964

During most of this period we did not have direct NASA support but the work continued in the same directions as before and as such, it seems appropriate to include it here.

Owing to the large number of people working under the contract this year a more diversified program was started and was still under way the summer of 1962. The optics and kinetics of simple impurity systems in alkali halides was again of continued interest this year. With new instrumentation, built over these past two years, new studies of photo emission and reflectivity could be started under much improved experimental conditions. A minor study with a ruby laser was started with the objective to learn the techniques of two-photon processes which later might prove useful for the optical study of alkali halides. This summer a new attempt was begun to study the photoconductivity of pure alkali halides. In more detail the following objectives were performed this year:

a) Absorption and Luminescence of Localized Excitons in Alkali Halides

The absorption and luminescence processes at iodine impurity centers in KCl single crystals was studied in previous years. The results of a detailed study of the various emission bands following the decay of these localized excitons was published: "Luminescent Decay of Localized Optical Excitations in KCl," Herbert Mahr, Phys. Rev. 130, 2257 (1963). In the realm of trying to understand in detail the processes during optical excitation and deexcitation of these single centers, hopefully in terms of a quantitative configurational

model (Franck-Condon model), more experimental parameters of this system were determined this year. The decay time of the bluegreen and the ultraviolet emission of the iodine centers was measured for a variety of samples of different concentrations and a wide temperature range. For this purpose a light source of short duration was built. The results of this study were presented at the Washington meeting of the American Physical Society (Bull. Am. Phys. Soc. 8, 353 (1963). The decay time of the bluegreen emission is very long (10^{-4} seconds at low temperature) and strongly temperature dependent. The decay time of the ultraviolet emission is short, about 10^{-7} seconds.

Two conclusions have been drawn from the detailed experimental study of these localized excitons. The existence of an appreciable exponential tail of the absorption band of the localized exciton has led to the proposal of a new shape formula: "Band Shape and Urbach's Rule of Localized Excitons," Herbert Mahr, submitted for publication in the Physical Review. It is suggested that the experimental observation of this exponential shape (Urbach's rule) is evidence of a quadratic interaction of certain lattice modes with the formation of localized excitons. The existence and influence of this type of local lattice modes has not been considered previously.

An attempt has been made to accommodate all the experimental results of this study in a quantitative configurational

model. It was found that a Franck-Condon model containing at least two configurational coordinates is necessary to reach agreement with all experimental findings. Although certain theoretical questions, which come up in connection with this three-dimensional Franck-Condon Model, have not been solved yet an attempt was made to construct quantitatively such a model. This model has been presented in an invited paper given at the Buffalo meeting of the American Physical Society (Bull. Am. Phys. Soc. 8, 433 (1963).

Localized excitons have proved to be a simple system for investigating optical processes. A study of the absorption of another such system has been started therefore this summer. KI has been added to KBr melt. The single crystals grown from this melt contain then iodine sites. The additional absorption due to these iodine centers is measured. The results obtained so far are of only preliminary nature, but agree with findings obtained with the system KI:KCl.

b) Kinetics, Photoconductivity and Phosphorescence of a Simple Impurity System in Alkali Halides (Duckett, Goldberg). It has been found -- while studying the optical excitation of localized excitons -- that phosphorescence and photoconductivity was observed at higher temperatures following absorption of light into the iodine absorption band of KCl. Negative ion vacancies in the KCl lattice were found to be the major traps. By addition of iodine ions to KCl single crystals a completely

symmetric impurity system has been created. Electrons, ionized from iodine ion sites by absorption of light plus subsequent thermal activation, are trapped at negative ion vacancies forming F-centers. Illumination with light absorbed in the F-band ionizes the trapped electrons again until they are finally trapped by ionized iodine ions. Experiments are under way to study the kinetics of this system extensively. This summer the F-center formation will be studied as a function of temperature.

c) New Instrumentation for Use with the Vacuum Ultra-Violet Monochromator and the Cary Model 14 Spectrophotometer.

Modulated Vacuum Ultraviolet Spectrograph: Work on the modulated spectrograph has been concluded. The results were fairly satisfactory but not really sensational, for the system is certainly more complicated than the simple fixed slit arrangement. It is feasible to eliminate the effect of scattered light for measurements in the extreme vacuum ultraviolet region of the spectrum with this arrangement, however, and for these it will probably be worth using. It will then be worth trying a new source to provide the short wavelength radiation others report using.

Ultra-High Vacuum System: A new ultra-high vacuum system was purchased and tried out in connection with reflectivity and photoemission studies. Presently it is tried to couple this ultra-high vacuum container with the vacuum ultraviolet

monochromator, thus allowing to perform ultra-high vacuum work (photoemission, etc.) in this region of the spectrum. This will constitute quite an improvement over currently used vacua of 10^{-6} mm Hg at the best.

Reflectometer: Work was completed this past winter on a cryostat reflectometer that was started three years ago primarily for studies on silver chloride. Fitted with an ion pump (ultra-high vacuum system), it was simple to make measurements at liquid helium temperature without deleterious condensation taking place on the sample surface. It is unique in that it can be fitted into the Cary Model 14 Spectrophotometer and allows absolute reflectivity to be obtained. A paper has been written and is to be published in October. Some thought is being given to an instrument in which the reflectivity as a function of angle of incidence may be obtained.

Polarizer: A polarizer for the Cary Spectrophotometer has been constructed and is being used successfully. A polarizer, consisting of LiF plates, useful for the vacuum ultraviolet region of the spectrum, has not yet been attempted. The block of LiF which was obtained to slice for this multi-plate polarizer has not yet been cleaved.

d) Photoemission and Reflectivity Studies. The work of Lloyd on the photoemission of LiF is being followed up this summer in an attempt to enclose the sample, an evaporated film of LiF, in something closer to an ultra-high vacuum system.

This is to slow down the process going on at the surface which is presumed to cause the long wavelength tail at the emission edge. In connection with the construction of the reflectometer, the region of the exciton absorption in AgCl was investigated. Measurements were performed in the temperature range from helium temperature to room temperature.

e) Two Photon-Processes (Ruby-Laser Work).

As a preliminary study for future optical work with two-photon processes the second harmonic generation of light in KDP has been reproduced. The whole setup of source (Ruby laser) and detection system has thus been proved to be ready for work to be started next year with two-photon stimulated luminescence and photoconductivity.